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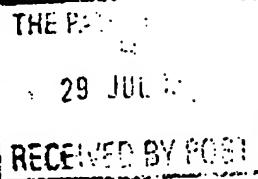
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29 JUL 96 E210207-1 004244
PO1/7700 25.00

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The Patent Office

Cardiff Road
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1. Your reference

High Efficiency EL Devices

2. Patent application number

(The Patent Office will fill in this part)

9615883.7

29 JUL 1996

3. Full name, address and postcode of the or of each applicant (underline all surnames)

CAMBRIDGE DISPLAY TECHNOLOGY LTD
181A Huntingdon Road
Cambridge CB3 0DS

06166441802 A
LLC

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

High Efficiency EL Devices

5. Name of your agent (if you have one)

PAGE WHITE & RAVEN

54 DOUGLASS STREET

LONDON

WC1N 2JB

Patents ADP number (if you know it)

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Country Priority application number
(if you know it) Date of filing
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Number of earlier application Date of filing
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Statement of inventorship and right to grant of a patent (Patents Form 7/77)
Request for preliminary examination and search (Patents Form 9/77)
Request for substantive examination (Patents Form 10/77)

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11.

I/We request the grant of a patent on the basis of this application.

Signature

Date July 26, 96

PAUL MAY
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12. Name and daytime telephone number of person to contact in the United Kingdom

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HIGH EFFICIENCY EL DEVICES

Field:

The field of the invention relates to the construction of organic light emitting diodes.

Background:

Organic electroluminescent devices are made from materials that emit light when a suitable voltage is applied across electrodes deposited on either side of the polymer. One class of such materials is semiconductive conjugated polymers which have been described in our earlier patent US, 5,247,190, the contents of which are herein incorporated by reference. Poly(p-phenylene vinylene) [PPV], for instance, will emit light when current is passed through the material by applying a voltage between two suitable electrodes. The electroluminescent efficiency of these devices is known to depend on the balancing of the electrons and holes that are injected into the device and meet to form electron/hole pairs, as well as on the efficiency with which these electron/hole pairs combine to radiate light i.e. the photoluminescence efficiency (eg see N.C. Greenham and R.H. Friend, Solid State Physics, 49, 1, 1995). Therefore it is of critical importance for an efficient device to have a high photoluminescence efficiency.

There are two different broad approaches to processing of conjugated polymers. One approach uses a precursor polymer which is soluble and can therefore be easily coated (eg by standard spin-coating and blade-coating techniques), but which is converted into its final form in situ eg by heat treatment to remove the solubilising side groups. The other approach uses directly soluble conjugated polymers which do not require a subsequent conversion stage. Depending on the specific application, one or other of the approaches might be relevant. The precursor polymer approach can be especially important where subsequent processing might lead to damage of the polymer film if it were directly soluble - such processing may be, for instance, coating with further polymer layers (eg transport layers or emitting layers of different colour), or patterning of the top electrode. Converted precursor films also have better thermal stability which is of importance both during fabrication but also for the storage and operation of devices at high temperatures.

Where the precursor polymer is converted to the final form by elimination or modification of a solubilising group it is generally important that these by-products of the conversion process are removed from the film. It may also be important that they do not interact with the substrate during this process, for example if this causes harmful impurities to move into the film thus affecting the performance (including luminescence efficiency and lifetime) of the electroluminescent device. We have observed, for instance, a quenching of the photoluminescence when precursor PPV polymers are converted on indium tin oxide. This is caused by indium being released into the PPV due to the interaction of one of the by-products of the conversion (hydrogen bromide) with the indium tin oxide.

The invention describes a device structure and a method of manufacture for an electroluminescent device that overcomes this problem.

Invention:

According to one aspect of the invention there is provided an electroluminescent device incorporating a converted precursor polymer as the emitting layer and an electrode protecting layer placed between the precursor and the underlying electrode and which acts to protect the electrode during the precursor conversion process, and a second electrode placed on the other side of the precursor polymer.

In one embodiment the electrode is formed from a layer of transparent conducting material deposited on glass or plastic, the transparent conducting material forming one of the electrodes of the device, typically the anode of the device. Examples of suitable anodes include tin oxide and indium tin oxide. Typical layer thicknesses are 500-2000A and resistivities are 10-100 ohm/square. The converted precursor polymer can be, for instance, poly(p-phenylene vinylene) [PPV] or a homopolymer or copolymer derivative of PPV. The thickness of this layer can be in the range 500-2000A. The substrate protecting layer is chosen to act as a barrier against the conversion by-products of the precursor polymer, but also must not act as a barrier to the injection of holes from the anode into the emitting layer, where they combine with electrons injected from the cathode to radiate light. Conducting polymers are a general class of materials that can combine ease of processing, protection of the underlying electrode, and suitable hole transporting and injecting properties and are therefore good candidates. Very thin layers (10-500 A) are used and therefore the transparency of the layer can be high. Typical resistivities of these layers are 100-1000 ohm/square. Examples include conjugated polymers that have been doped including polythiophenes and their derivatives and polyanilines. The cathode electrode is placed on the other side of the converted precursor material and completes the device structure.

In another embodiment the electrode protection layer and the precursor polymer is deposited on the cathode, typically a material such as aluminium or an alloy of aluminium with a low work function element or any low work function element or alloy. In this case the protection layer will need to transport electrons, but will not need to be transparent. Again conducting polymers are suitable candidates as electrode protection layers. The anode electrode is placed on the other side of the converted precursor material and completes the device structure.

In yet another embodiment a protection layer to either the anode or cathode as described above is provided, but where the protection layer is an undoped conjugated polymer but which has sufficient injection properties and transport mobilities for either holes or electrons depending on whether it is protecting the anode or cathode respectively. An example of such a protection layer would be a soluble PPV derivative or alternatively a precursor PPV or PPV derivative material. In the latter case, because the protection layer is typically much thinner than the electroluminescence layer, the by-products of the conversion process are more easily removed and therefore any interaction with the electrode during conversion is minimised.

In yet another embodiment a protection layer to either the anode or cathode as described above is provided, but where the protection layer is an evaporated or

sputtered thin film which has sufficient injection properties and transport mobilities for either holes or electrons depending on whether it is protecting the anode or cathode respectively. An example of such a protection layer would be a thin layer of evaporated carbon, a sputtered layer of amorphous silicon or a sublimed organic semiconductor layer.

In yet another embodiment a protection layer to either the cathode or anode as described above is provided, but where the protection layer is an undoped polymer but which has sufficient injection properties and transport mobilities for either holes or electrons depending on whether it is protecting the anode or cathode respectively. An example would be polyvinyl carbazole which is a good hole transporting material but is not a conjugated polymer. Alternatively very thin layers of polymer materials which have relatively poor hole and electron mobilities may function as good electrode protectors without compromising the balance of electron and hole charge carriers. An example would be polystyrene.

In yet another embodiment a protection layer to either the cathode or anode as described above is provided, but where the protection layer is a very thin dielectric which provides a barrier to the precursor conversion by-products, but which is thin enough that holes can tunnel through it when it is in contact and protecting the anode or electrons can tunnel through it when it is in contact and protecting the cathode.

A second aspect of the invention provides a method of manufacture of an electroluminescence device wherein a precursor to a conjugated polymer material is deposited on a substrate on which has previously been deposited both an electrode layer and subsequently an electrode protection layer. The precursor is then converted to the final conjugated polymer form before deposition of a subsequent layer or layers at least one of which is the second electrode.

Drawing:

Figure 1. Electroluminescent device structure incorporating an electrode protection layer.

Figure 2. Conversion route of a standard PPV precursor.

Specific Embodiment:

A specific embodiment is now described. Indium tin oxide is deposited using either dc or rf sputtering techniques onto polished glass substrates. Such substrates are available commercially. Typical products use soda lime glass with a thin silica barrier and an indium tin oxide layer of resistivity 30 ohm/square and transparency of about 85%, with a thickness of order 1500A. A polythiophene based conducting polymer system is used as a protection layer - Polyethylene dioxythiophene polystyrene sulphonate (PEDT/PSS) - which is available from Bayer as Trial Product AI 4071. A 100A film of the conducting polymer is spin-coated on the substrate before spin-coating the precursor polymer which is typically a PPV copolymer developed by us. This material has a very high photoluminescence (PL) efficiency, where the solubilising group that is removed during conversion is tetrahydrothiophene, and the counter-ion to the thiophene salt is bromine. Another by-product is therefore hydrogen bromide which readily attacks ITO and can

release indium into the film which quenches the photoluminescence. Without the protector layer, the PL efficiency and therefore the EL efficiency of the PPV material is dramatically reduced from over 65% to about 20% following the thermal conversion process - 150C in nitrogen for 4 hours. However, with the protector layer the PL efficiency is only slightly reduced following conversion. After the conversion a suitable cathode material, calcium for instance, is deposited on top of the conjugated polymer. The final device structure is indicated in Figure 1 and the conversion by-products of the PPV-based precursor are indicated in Figure 2. Devices made with the protector layer typically have 10x higher electroluminescence efficiency compared to the devices without the protector layer.

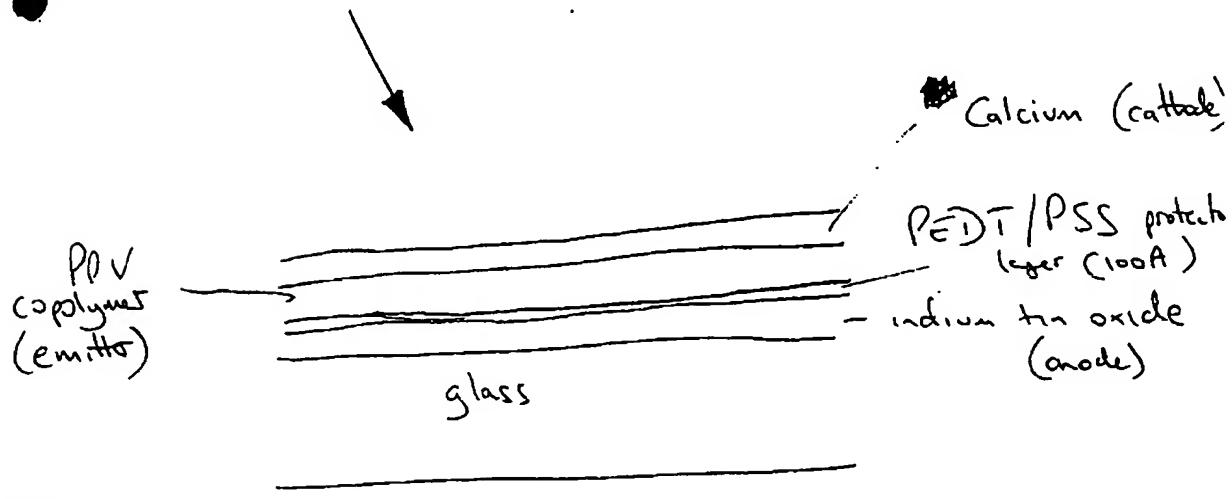


FIGURE 1

Schematic of
device layer structure

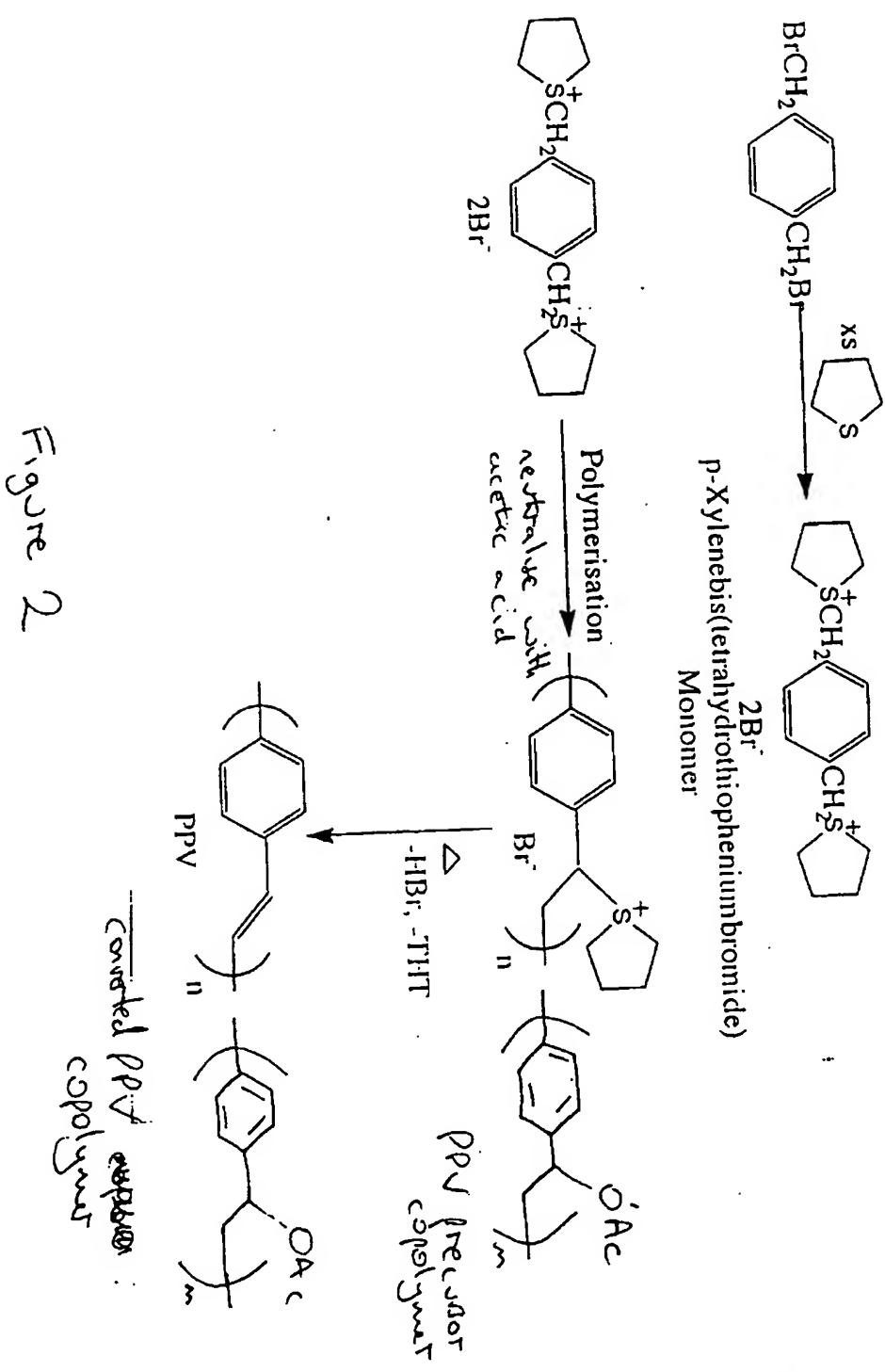


Figure 2